

BRODSKIY, A.I. and MIKLUKHIN, G. P.

"Investigation of the mechanism of sulphur compound reactions and of sulphur isotope exchange," a paper submitted at the International Conference on Radioisotopes in Scientific Research, Paris, 9-20 Sep 57.

KROCKIY, H. I.

Call Nr: AF 1145611

AUTHOR:

Brodskiy, A. I.

'TITLE:

Chemistry of Isotopes (Khimiya izotopov)

PUB. DATA:

Izdatel'stvo Akademii nauk SSSR, Moscow, 2nd ed.,

1957, 595 pp., 7,000 copies

ORIG. AGENCY: Akademiya nauk SSSR. Otdeleniye khimicheskikh nauk.

EDITOR:

Katrenko, D. A.

PURPOSE:

This is a reference book for chemists, research chemists, teachers, and engineers as well as for

specialists in other fields of science and technology,

namely, physics, biology, medicine, agricultural chemistry, etc. The author's purpose was to give a brief historical review of the chemistry of isotopes and to bring up to date the development of isotopy by covering Soviet and non-Soviet monographs and

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Chemistry of Isotopes. (Cont.)

periodicals. Separation and analysis of isotopes and use of isotopes in chemistry, geochemistry, biology, and agriculture are discussed at length.

COVERAGE:

The first edition was published in 1952. In the second edition the following chapters were completely revised: Ch. 4, Analysis of Stable Isotopes, pp. 105-143, Ch. 5, Radioactive Isotopes, pp. 144-233, Ch. 7, Isotope Exchange Reactions, pp. 283-353,

Ch. 8, Mechanism of Chemical Reactions, pp. 354-424, and Ch. 9, Use of Isotopes in Chemical Analysis, Industry, and Agriculture, pp. 425-490. The use of isotopes in physical chemistry is stressed. The number of references in the second edition (1957) is 1556, 452 of which

are USSR.

AVAILABLE:

Library of Congress

CARD: 2/2

BRODSKIY, A.I.; VYSOTSKAYA, N.A.

Oxygen exchange in inorganic acids and salts. Probl. kin. i kat. 9: 245-250 *57. (MIRA 11:3) (Acids) (Salts) (Oxygen--Isotopes)

BRODSKIY, A. I.

Discussion. Probl. kin. i kat. 9:275 '57. (MIRA 11:3)

(Catalysis)

BRODSKIY, A.I.

Relationship between kinetic isotope effect and change of isotope content during the course of the reaction. Probl. kin. i kat. 9: 360-362 57. (HIRA 11:3 (Chemical reaction, Rate of) (Isotopes)

BRODSKIY, S.Z.; BRODSKIY, A.I.; VARSHAY_IY, Ya.M.

Discussion. Probl. kin. i kat. 9:369-370 '57. (MIRA 11:3)

(Chemical reaction, Rate of) (Isotopes)

BRODSKIY, A.I.; KALINENKO, R.A.; LAVROVSKIY, K.P.

The application of adsorbtion method of analysis and separation of hydrocarbon gases during kinetic study using labeled atoms. Probl. kin. 1 kat. 9:399-404 157. (MIRA 11:3) (Gases--Spectra) (Carbon--Isotopes)

Brodskiy A.l.

AUTHOR:

Brodskiy, A. I., Corresponding Member of the Academy,

Franchuk, I. F., and Lumenok-Burnakina, V. A.

TITLE:

The Study of the Mechanism of the Electrolytic Formation and

Hydrolysis of Persulfates by the Isotopic Method

(Izucheniye mekhanizma elektroliticheskogo obrazovaniya i gidro-

liza persul'fata izotopnym metodom)

PERIODICAL:

Doklady Akademii Nauk SSSR, 1957, Vol. 115, Nr 5, pp. 934 - 937

(USSR)

ABSTRACT:

Various mechanisms, which had been recommended for the anodic formation of persulfates by sulfate electrolysis can be classed into 2 types: 1.) According to the most usual conceptions, persulfate is formed by a direct recombination of the discharging sulfate- (or bisulfate-) ions. 2.) According to other opinions water oxidation products (H₂O₂, OH, OH, surface oxides, etc.) are formed primarily on the anode or in the electrolytic layer near the anode, which then oxidize the sulfate by electron or exygen atoms. Most of the other mechanisms suggested belong to one of the two types, differing only with respect to details of

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the intermediate stages. Frumkin and his collaborators proved that in the electrolysis of a K_2SO_4 solution in H_2O^{18} in an acid, neutral, or slightly alkaline medium persulfate oxygen is free from surplus heavy oxygen. This makes it possible to reject all those mechanisms in which the participation of water oxygen in the formation of persulfates is presumed. The authors made use of the heavy oxygen isotope in order to clarify the problem of a possible participation of hydrogen peroxide in the anodic formation of persulfates and for the study of the mechanism of persulfate hydrolysis. It was already known that H202 and K2S208 exchange no oxygen with water. Solutions of 40 g KHSO, were subjected to electrolysis in 200 ml water through a current of 3 A between platinum electrodes at 10 - 15 . Results: 1.) The persulfate yeald decreased abruptly if 10 - 20 g/1 H₂O₂ was added to the electrolyte. It then increased in accordance with the decrease of the not decomposed remainder of H202. The two anode processes H₂O₂ - decomposition and formation of K₂S₂O₈ apparently take place independently. The intermediate formation of H₂O₂ is doubted. The independence of the two anode processes is confirmed by the electrolyte experiments of KHSO, + H2O2 in

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H₂0¹⁸ with an isotopic analysis of the anodic oxygen (table 1). Also the results obtained by these experiments show that the anodic oxidation of H₂0₂ take place without the participation of water-oxygen. 2.) In order to prove definitely that H₂0₂ does not participate in the anodic formation of persulfate, the authors employed the method of isotopic dilution. It may be seen from all results obtained that neither H₂0₂ nor, apparently the OH radicals can be intermediate product of persulfate formation on the anode, because the former recombine quickly in H₂0₂ by exchanging their oxygen with water. 3.) A mixture of 1,3 - 4 g K₂S₂O₈ with 1 - 3 g 70% HClO₄ or 50% H₂SO₄ was hydrolized at 70 by blowing through steam at 30 torr. As seen from table 3, H₂O₂ had the composition of the water if H₂O₁₈ was used. Thus, the entire oxygen of the H₂O₂ originates from the persulfate oxygen without the participation of water oxygen. In all cases, also in the case of previous works, it was proved that the peroxide bridge is not interrupted and that water oxygen is not incorporated within the decomposition products of (also other) peroxides. A comparison of the data obtained from the authors

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shows that in the sequence of transformations

S₂0₈ ---> S₀ ---> H₂0₂ ---> O₂ the peroxide group -0-0- goes over from the persulfate, without undergoing separation, into the final product of its decay, i.e. oxygen. In order to eliminate the secondary exchange between HSO_A or of the H₂SO_A produced therefrom and water, Pb (ClO_A)₂ was added. This was not fully effective although the exchange became less. This proved that a considerable quantity of O¹⁸ is introduced into the bisulfate by secondary exchange. This agrees with the scheme mentioned though it still lacks quantitative confirmation. There are 1 figure, 3 tables, and 5 Slavic references.

ASSOCIATION:

Institute for Physical Chemistry imeni L.V. Pisarzhevskiy AN Ukrainian SSR (Institut fizicheskoy khimii im. L.V.Pisarzhevskogo Akademii nauk USSR)

SUBMITTED:

March 13, 1957

AVAILABLE:

Library of Congress

Card 4/4

BRODSKIY, A. I., VYSOTSKAYA, N. A., KUKHTENKO, I. I., MIKLUKHIN, G. P. (Deceased) STRIZAK, L. L., and SULIMA, L. V. (Inst. of Phys. Chem. im. L. V. Pisarzhevskiy, Acad. Sci. Uk. SSR.

"Isotopic Exchange of Oxygen, Nitrogen, and Sulfur in Solutions, and Its Mechanism."

Isotopes and Radiation in Chemistry, Collection of papers of 2nd All-Union Sci. Tech. Conf. on Use of Radioactive and Stable Isotopes and Radiation in National Economy and Science, Moscow, 12d-vo AN SSSR, 1958, 380pp.

This volume published the reports of the Chemistry Section of the 2nd AU Sci Tech Conf on Use of Radioactive and Stable Isotopes and Radiation in Science and the National Economy, sponsored by Acad Sci USSR and Main Admin for Utilization of Atomic Energy under Council of Minimsters USSR Moscow 4-12 Apr 1957.

BRODSKIY, A.I., akademik

Isotopic exchange. Khim.nauka i prom. 4 no.4:423-434 '58.

(MIRA 13:8)

1. Akademiya nauk USSR.

(Isotopes)

AUTHOR:

Brodskiy, A. I.

SOV/89-5-1-5/28

TITLE:

The Use of Isotopes in the Investigation of the Chemical Structure and of the Reaction Mechanism (Primeneniye izotopov k izucheniyu khimicheskogo stroyeniya i mekhanizma reaktsiy)

PERIODICAL:

Atomnaya energiya, 1958, Vol. 5, Nr 1, pp. 52-63 (USSR)

ABSTRACT:

The basic methods employed when using radioactive indicators are given (as described in a paper). The methods employed when investigating the chemical structure, especially of organic substances, and the investigation of the mechanism of chemical reactions are explained. The following methods are described:

1.) Using isotopes for the marking of atoms.

2.) Investigation of isotope exchange.3.) Use of radioisotopic dilution.

4.) Measurement of the kinetic isotope effect.

Each of these methods is illustrated by means of an example taken from the various fields of chemistry; reference is also made to work carried out in the author's laboratory. There are

52 references, 32 of which are Soviet.

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The Use of Isotopes in the Investigation of the Chemical Structure and of the Reaction Mechanism

SOV/89-5-1-5/28

SUBMITTED:

July 22, 1957

1. Radioisotopes—Applications 2. Radiochemistry 3. Chemical reactions—Analysis 4. Structural analysis

Card 2/2

AUTHORS:

Brodskiy, A. I., Vysotskaya, N. A.

sev/76-32-7-12/45

TITLE:

The Isotopic Exchange of Oxygen in Acid and Salt Solutions and Its Mechanism (Izotopnyy obmen kislorode v rastvorakh

kislot i soley i yego mekhanizm)

PERIODICAL:

Shurnal fizicheskov khimii, 1958, Vol. 32, Nr 7, pp. 1521-1531

(USSR)

ABSTRACT:

From the existing data in publications, intrite of the great amount of information no rule governing the exchange mentioned above can be found, as the investigations were carried out to a great extent only qualitatively and under insufficient conditions. Several assumptions as regards the reaction mechanism are found; among them especially those are worth mentioning according to which the exchange takes place the more easily the greater the ion share of the compound is, i.e., the higher the difference between the electronegativities of oxygen and that atom is to which it is bound. In cases where the exchange took place at measurable rates the kinetics of the process were investigated. L. V. Sulima and A. I. Brodskiy (Ref 15) investigated the reaction mechanism suggested in their earlier publication for this case, and later proved it in a subsequent publication. From the experimental part may be seen that a

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number of salts and acids dissolved in water mainly of the elements of the groups V, Vl, and TII, with the isotopic composition of the water being determined prior to and after the experiment according to a flotation method described. In some determinations a less precise make-spectrometric method ass employed. The measurements of the exchange kinetics carried out correspond to an ordinary isotopic exchange according to an equation of first order, the ratio k/k, being within the range 35-55. From the experimental results obtained may be seen that in the nitrates investigated the exchange velocities depend on the cation and on the acidity of the solution; further measurements with some substances showed the inaccuracy of the data existing in publications. According to the data supplied by Edwards (Ref 30) and Hall and Alexander (Ref 3) it was found that the exchange velocity in the series acid > acid salt > neutral salt drops abruptly; the corresponding examples are given. On the other hand it, was found in a comparison of acids and salts with the same central atom that the exchange velocity is reduced sharply by an increase of the number of oxygen atoms (or of sulfur) bound to this central atom. Within the range of the subgroups of the periodic system

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table the exchange velocity increases with the increase of the atomic number of the central atom. The rules observed are explained by the mechanism of an intermediate deposition of water to the double bond X=0 (or X/-0), with an introduction of the hydrolytic mechanism being possible. The data supplied by S. Z. Roginskiy (Ref 29) are incorrect. There are 2 figures, 5 tables, and 33 references, 12 of which are Soviet.

ASSOCIATION:

Akademiya nauk USSR, Institut fizicheskoy khimii im. L. V. Pisarzhevskogo (Institute of Physical Chemistry imeni L. V. Pisarzhevskiy, AS Ukr SSR)

SUBMITTED:

March 1, 1957

Oxygen-Exchange reactions
 Exchange reactions-Velocity
 Hydrogen ion concentration-Chemical effects
 Salt solutions

Card 3/3

BRODSKIY, A. l.

AUTHORS:

Franchuk, I. F., Brodskiy, A. I., Corresponding 20-1-36/58
Member of the AN USSR.

TITLE:

The Use of the Isotopic Method in Studying the Mechanism of Electrolytic Formation and Decomposition of Percarbonate, Perborate and Perphosphate (Izucheniye mekhanizma elektro-liticheskogo obrazovaniya i razlozheniya perkarbonata, perborata i perfosfata izotopnym metodom).

PERIODICAL:

Doklady AN SSSR 1958, Vol. 118, Nr 1, pp. 128-130 (USSR)

ABSTRACT:

In the present work the heavy oxygen isotope 0^{18} is used for the study of the mechanism of the anodic production, of hydrolysis as well as of the thermal decomposition of percarbonate, perborate and perphosphate. Potassium percarbonate $K_2C_2O_6$ was produced by means of the electrolysis of from 20 to 30 g of K_2CO_3 in 50 milliliters H_2O^{18} with a current of from 1,2 to 2 a between platinum electrodes at a temperature of from -10 to -14° in the cell. The further treatment of the electrolyte samples is shortly shown. The result of such an experiment as well as of the electrolysis of $K_2CO_3^{18}$ are mentioned in a table. The isotope composition of oxygen in CO_2 and in O_2 is similar to the composition in the original carbonate. This

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The Use of the Isotopic Method in Studying the Mechanism of Electrolytic Formation and Decomposition of Percarbonate, Perborate and Perphosphate.

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excludes a participation of water in the production of percarbonate. An electrolytic production of percarbonate with essential yields occurs only in the presence of carbonate. For the purpose of the explanation of the mechanism of this process the authors made a number of analysis of the solutions of 4g Na₂B₄O₇ + 12 g Na₂CO₃ in 100 milliliters of H₂O¹⁸ as well as of the solutions Na₂B₄O₇ +Na₂CO₃¹⁶ in ordinary water at +10 -14° with a current of from 2-3 a between a platinum anode and a Sn cathode. The results of two such experiments are shown in a table. According to this CO₂ and O₂ of the electrolyte as well as O₂ of the perborate have a similar content of O¹⁸ which is much smaller than with water. This excludes a participation of water-oxygen in the production of perborate. These and other data show that the primary electrode process is the production of the percarbo-

nate. The perborate obtained by means of the electrolysis is formed through a compound of $\rm H_2O_2$. Then the authors report

on the electrolytic production of potassium perphosphate

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The Use of the Isotopic Method in Studying the Mechanism of Electrolytic Formation and Decomposition of Percarbonate, Perborate and Perphosphate.

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 $K_{4}P_{2}O_{8}$; it obviously is formed after the reaction

 $2P0_4^{3-} \rightarrow P_20_8^4 + 2e$. With the hydrolysis of percarbonate, perborate and perphosphate the peroxide group 0-0 moves over to the developing H_20_2 in undestroyed condition. The thermal decomposition of percarbonate and perborate in H_20^{18} supplies, as was expected, oxygen of normal isotope composition. There are 1 figure, 3 tables, and 8 references, 1 of which is Slavic.

ASSOCIATION: Institute for Physical Chemistry imeniL. V. Pisarzhevskiy AN Ukrainian SSR (Institut fizicheskoy khimii imeni L. V.

Pisarzhevskogo Akademii nauk USSR).

SUBMITTED: August 12, 1957

AVAILABLE: Library of Congress

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5(4) AUTHORS:

Brodskiy, A. I., Corresponding Member, SOV/20-123-1-31/56 Academy of Sciences, USSR, Franchuk, V. I., Aleksankin, M. M., Lunenok-Burmakina, V. A.

TITLE:

Investigation of the Reactions of the Production of Hydrogen Peroxide in the Oxidation of 2-Ethyl Antrahydroquinone and Isopropanol by the Isotope Method (Issledovaniye reaktsiy obrazovaniya perekisi vodoroda pri okislenii 2-etilantragidrokhinona i izopropanola izotopnym metodom)

PERIODICAL:

Doklady Akademii nauk SSSR, 1958, Vol 123, Nr 1, pp 117-119 (USSR)

ABSTRACT:

The mechanism of the reactions serving as a basis of the industrial methods of producing hydrogen peroxide by the oxidation of 2-ethylantrahydroquinone (or its derivatives) and of isopropyl alcohol by elementary oxygen has hitherto not been investigated. For the purpose of solving this problem the authors investigated the above-mentioned reactions by means of the isotopic method. 1) The oxidation of 2-ethyl hydroquinone and tetrahydro-2-ethyl antrahydroquinone was carried out under conditions similar to those employed in industry. The results obtained by experiments carried out with a mixture 1: 1 of the

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Investigation of the Reactions of the Production of SOV/20-123-1-31/56 Hydrogen Peroxide in the Oxidation of 2-Ethyl Antrahydroquinone and Isopropanol by the Isotope Method

aforementioned substances (working mixture) are given in a table. According to the data of this table, the oxygen of the produced hydrogen percuide originates entirely from the elementary oxygen used for oxidation. The oxygen of the hydroxyl groups of antrahydroquinone or of alcohol does not take part in the reaction. The mechanism

$$(CH_3)_4^{C_6}(OH)_2 \rightleftharpoons (CH_3)_4^{C_6}(OH_3)_5^{C_6}(OH_3)_5^{C_6}(OH_3)_5^{C_6}(OH_3)_5^{C_6}(OH_3)_5^{C_6}(OH_3)_5^{C_6}(OH_3)_5^{C_6}(OH_3)_5^{C_6}(OH_3)_5^{C_6}(OH_3)_5^{C_6}(OH_3)_5^{C_6}(OH_3)_5^{C_6}(OH_3)_5^{C_6}(OH_3)_5^{C_6}(OH_3$$

suggested by R. B. Weissberger (Veysberger) et al. (Ref 2) is hardly probable in the reactions under investigation. Also the intermediate production of transannular peroxides can be excluded. Mechanisms with intermediate production of hydrogen peroxides or radical mechanisms with stripping of a proton from the hydroxyl of the antrahydroquinone are compatible with the results obtained by the aforementioned experiments. For the purpose of further clarification of the mechanism of the reactions investigated, the authors introduced deuterium into the hydroxyl groups of the 2-ethyl antrahydroquinone by the

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Investigation of the Reactions of the Production of SOV/20-123-1-31/56 Hydrogen Peroxide in the Oxidation of 2-Ethyl Antrahydroquinone and Isopropanol by the Isotope Method

exchange with methyl alcohol CHzOD. Carrying out of this reaction is described in short. The hydrogen in the H₂O₂ obtained originates entirely from the hydroxyl groups of the ethyl antrahydroquinone. According to these data it is possible to exclude also the intermediate production of hydrogen peroxide with addition of the peroxide group into any position (with the exception of 9 or 10). The formation of the hydrogen peroxides in the positions 9 or 10 is not contradictory to the abovediscussed observations. By the authors' request V. V. Voyevodskiy, N. N. Bubnov, and N. I. Tikhomirovarecorded the spectrum of a solution of 2-ethyl antrahydroquinone during its oxidation. On this occasion the radical semiquinone was not found. In higher concentrations of a basic medium a distinct spectrum of the radical ion semiquinone was found. Several secondary alcohols are known to oxidize easily by elementary oxygen. In this connection the authors oxidized isopropyl alcohol, in which case the hydrogen peroxide yield amounted to 48%. Also in this case

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Investigation of the Reactions of the Production of SOV/20-123-1-31/56 Hydrogen Peroxide in the Oxidation of 2-Ethyl Antrahydroquinone and Isopropanol by the Isotope Method

the entire oxygen of hydrogen peroxide originates from elementary oxygen, and the oxygen in the hydroxyl of the alcohol does not participate. There are 1 table and 6 references.

ASSOCIATION: Institut fizicheskoy khimii im. L. V. Pisarzhevskogo Akademii nauk USSR (Institute for Physical Chemistry imeni

L. V. Pisarzhevskiy of the Academy of Sciences, UkrSSR)

SUBMITTED: June 21, 1958: :

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SOV/25-59-5-4/56

AUTHOR:

Brodskiy, A. I., Academician

TITLE:

Isotopes in Chemistry

PERIODICAL:

Nauka i zhizn', 1959, No. 5, pp 6-10 (USSR)

ABSTRACT:

The author of this article, a well-known Soviet physicist and chemist, Member of the AS Ukrainian SSR, Corresponding Member of the AS USSR, Winner of the Stalin Prize and Director of the Institut fizicheskoy khimii imeni L.V. Pisarzhev-skogo (Institute of Physical Chemistry imeni L.V. Pisarzhev-skiy) of the AS UkrSSR in Kiyev, explains the nature of isotopes and their fields of application, e.g. with atomic power engineering, as sources of radiation, and their utilization as marked atoms. The author deals in detail with the last item, describing the use of marked atoms with chemical reactions, in analytical chemistry and biochemistry. There are

ASSOCIATION:

2 photos and 2 drawings.
Institut fizicheskoy khimii im. L. V. Pisarzhevskogo Akademii nauk Ukrainskoy SSR (Institute of Physical Chemistry imeni L.V. Pisarzhevskiy, Ukrainian Academy of Sciences), Kiyev.

Card 1/1

5(4) AUTHORS:

Strizhak, L. L., Demidenko, S. G., SOV/20-124-5-36/62

Brodskiy, A. I., Corresponding Member, AS USSR

TITLE:

The Isotopic Exchange of Nitrogen Between Aminocompounds and Liquid Ammonia (Izotopnyy obmen azota mezhdu aminosoyedineni-

yami i zhidkim ammiakom)

PERIODICAL:

Doklady Akademii nauk SSSR, 1959, Vol 124, Nr 5, pp 1089-1092

(USSR)

ABSTRACT:

The present paper contains a report about new results obtained by a closer investigation of the kinetics of exchange and its oxygen catalysis. These new data fully agree with the exchange mechanism already previously assumed. The experiments were carried out in thick-walled ampoules made from molybdenum glass and having an inner diameter of 2-3 mm. Experiments are described in short. A table shows the results obtained for acetamine and benzamine. A further table and 2 diagrams show (though less accurately) the results obtained for other substances. Short reference is made to measurements previously carried out. According to exact measurements, liquid ammonia exchanges no nitrogen with the nitro group, with the nitrogen of the pyridine ring and (which is the most essential fact in

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The Isotopic Exchange of Nitrogen Between Aminocompounds and Liquid Ammonia

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the present case) with the amino group if it is immediately connected with the carbon of the aromatic nucleus or alkyl. Exchange in the amino group takes place during the exchange of highly negative substituents (such as the nitro- or sulfogroups) into the nucleus. Several details are mentioned. A relatively rapid exchange occurs in substances in which the amino group is immediately connected with the highly polarized carbon of the carbonyl groups or with groups analogous to the latter. Exchange is considerably accelerated by the presence of an ammonium ion. All characteristic features of nitrogen exchange in amino-compounds investigated in this paper agree fully with the bimolecular mechanism (SN2) of the nucleophile substitution of the amino group of the substance to the amino-group of ammonia with transfer of the proton from the last-mentioned group to the amino-group to be split off. There are 2 figures, 2 tables, and 5 references, 3 of which are Soviet.

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The Isotopic Exchange of Nitrogen Between Aminocompounds and Liquid Ammonia

SOV/20-124-5-36/62

ASSOCIATION:

Institut fizicheskoy khimii im. L. V. Pisarzhevskogo Akademii

nauk USSR (Institute for Physical Chemistry imeni L. V.

Pisarzhevskiy of the Academy of Sciences, UkrSSR)

SUBMITTED:

November 3, 1958

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5.2600(A)

68171

sov/20-129-6-38/69

AUTHORS:

Lunenok-Burmakina, V. A., Brodskiy, A. I., Academician,

AS UkrSSR

TITLE:

Investigation of the Mechanism of the Oxidation of Some In-

organic Substances by Persulfate

PERIODICAL:

Doklady Akademii nauk SSSR, 1959, Vol 129, Nr 6, pp 1335-1338

(USSR)

ABSTRACT:

The authors refer to the various opinions expressed in publications on the reaction of peroxides (Refs 2-13), among others to one of their own, which was elaborated in collaboration with I. F. Franchuk (Ref 1). For the purpose of explaining what happens in the reaction ${\rm K_2S_2^0_8} + {\rm H_2O_2} \longrightarrow {\rm 2KHSO_4} + {\rm O_2}$, the following three systems differently tagged by 018 were

investigated: $K_2S_2^{08} + H_2^{02} + H_2^{03}$; $K_2S_2^{08} + H_2^{02} + H_2^{03}$

 $K_2S_2O_8 + H_2O_2 + H_2O_5$. The liberated oxygen was investigated by means of spectroscopic analysis as to its 0^{18} content. The

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Investigation of the Mechanism of the Oxidation of Some Inorganic Substances by Persulfate

investigation of the 0¹⁸ content of other substances has already been described by reference 1. Table 1 shows that the liberated oxygen has the same isotopic composition as H₂O₂,

that the oxygen of bisulfate formed has the composition of persulfate, and that the oxygen of water does not take part in the reaction. The change of the acidity of the medium had no influence on the reaction. Further, the following reactions were investigated: 1) $K_2S_2O_8 + 2AgNO_3 + 2H_2O \longrightarrow Ag_2O_2 +$

+ 2KHSO₄ + 2HNO₃. Here AgO* was formed only from H₂O*, whereas O¹⁸ contained in K₂S₂O₈ passes over completely into the bisulfate. The oxidation of Ag thus takes place according to the electron mechanism without a transfer of oxygen. AgO is no real peroxide. 2) The same result was obtained in the reaction

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MnCl₂ + $K_2S_2O_8$ + $3H_2O \longrightarrow H_2MnO_3$ + $2KHSO_4$ + 2HCl, and the difference in the binding of the three O-atoms in H_2MnO_3 was confirmed (Ref 18). One of the O-atoms is easily exchangeable so that the formula $MnO_2 \cdot H_2O$ is more correct. 3) The reaction $K_2S_2O_8$ + PbS \longrightarrow PbSO₄ + K_2SO_4 + S was carried out with a solution of not tagged persulfate in water tagged with O^{18} . The oxygen of water did not react. Also in this case the PbS is oxidized by the persulfate according to the electron mechanism. This was confirmed by experiments with PbS which was tagged with S^{55} . The liberated sulfur contained the entire S^{55} , whereas PbSO₄ and K_2SO_4 were not active. Unlike the oxidation with H_2O_2 , that with persulfate was accompanied in all reactions investigated by a separation of the -O-O- bond, and takes place by a transfer of electrons, but not of O-atoms from the oxidizing substance to the substance to be oxidized. The authors

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> thank A. P. Potemskaya, E. G. Veselaya, and T. A. Vovk for their collaboration. There are 1 table and 19 references, 5 of which are Soviet.

ASSOCIATION: Institut fizicheskoy khimii Akademii nauk USSR

(Institute of Physical Chemistry of the Academy of Sciences

of the Ukrainskaya SSR)

SUBMITTED: September 5, 1959

Card 4/4

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S/CC1/62/000/001/004/067 B156/B101

AUTHORS:

Brodskiy, A. I., Gragerov, I. P., Franchuk, I. F., Sulima, L.V., Kukhtenko, I. I., Lunenok, V. A., Fomenko, A. S.,

Aleksankin, M. M.

TITLE:

Mechanism of oxidation reactions investigated by the isotopic

method

PERIODICAL:

Referativnyy zhurnal. Khimiya, no. 1, 1962, 60, abstract 1B439 (Tr. Tashkentsk. konferentsii po mirn. ispol'zovaniyu etomn. energii, v. 2. Tashkent, AN UzSSR, 1960, 327-334)

TEXT: A review of work done by the authors on studying the mechanism of certain oxidation reactions using isotopes: the oxidation of organic compounds with chromyl chloride, the mechanism of anthranil regrouping, the process of oxidation of aniline, o-anisidine and p-nitroaniline with Caro acid. The mechanism whereby hydrogen peroxide and certain persulfate-type inorganic peroxide compounds are formed and converted is examined; so also are the kinetics of isotopic exchange in substituted benzoic acids.

Card 1/2 South Proposal Chem AS USSK

Mechanism of oxidation reactions ...

S/081/62/000/001/004/067 B156/B101

benzaldehydes, alcohols, naphthalenes and nitro compounds with ${\rm H_20}^{18}$. 18 references. [Abstracter's note: Complete translation.]

Card 2/2

GORDIYENKO, L.L.; BRODSKIY, A.I.

Isotopic exchange of nitrogen in amides of acids. Dokl. AN SSSR 134 no.3:595-598 S '60. (MIRA 13:9)

1. Institut fizicheskoy khimii im. L.V. Pizarzhevskogo Akademii nauk USSR. 2. Chlen-korrespondent AN SSSR (for Brodskiy).

(Nitrogen-Isotopes) (Amides)

BRODSKIY, A.I.; GOL'DENFEL'D, I.V.

Verifying the accuracy of age determination by the lead-isotope methods. Biul.Kom.po opr.abs.vozr.gool.form. no.4:98-108 '61. (MIRA 15:1)

(Geological time) (Lead-isotopes)

LUNENOK-BURMAKINA, V.A.; POTEMSKAYA, A.P.; BRODSKIY, A.I.

Mechanism of the anodic formation of ozone from sulfuric acid solutions. Dokl. AN SSSR 137 no.6:1402-1404 Ap '61. (MIRA 14:4)

- 1. Institut fizicheskoy khimii imeni L.V.Pisarzhevskogo AN USSR.
- 2. Chlen-korrespondent AN SSSR (for Brodskiy). (Ozone)

"APPROVED FOR RELEASE: 06/09/2000

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25337

15.2230 (3309, 1413, 3009

21.4100

S/020/61/138/006/013/019 B103/B215

AUTHORS:

Brodskiy, A. I., Corresponding Member AS USSR, and

Franchuk, I. F.

TITLE:

Investigation of higher oxides and peroxides of uranium by

the isotope method

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 138, no. 6, 1961, 1345-1348

TEXT: The authors studied the system U-0 below $400^{\circ}\mathrm{C}$ at a ratio of 0:U=2.67 to 4. So far, this system has only been studied in detail at higher temperatures and at a ratio of 0:U=1:3 in solid phase. The authors assume the existence of the stoichiometric oxides U0, U0₂, U₃0₈, and U0₃. The peroxide U0₄°2H₂0 from which the peroxide U₂0₇ is obtained by thermal decomposition has also been known for a long time, although its structure so far has not been clarified. For their studies the authors used the radioactive 0¹⁸ which was introduced into various positions of the initial U0 °2H₂0, U0₄°2H₂0 was then slowly decomposed in vacua at temperatures

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25337 \$/020/61/138/006/013/019 B103/B215

Investigation of higher exides and ...

up to 700°C. The peroxide $\rm UO_4^{18} \cdot 2H_2O$ containing $\rm O^{18}$ only in the peroxide oxygen was precipitated from a solution of $\rm UO_2(NO_3)_2$ in water with heavy $\rm H_2O_2^{18}$ at room temperature, or by heating up to 90°C. $\rm UO_4 \cdot xH_2O^{18}$ was produced by transforming newly precipitated $\rm UO_4 \cdot xH_2O$ with $\rm H_2O^{18}$, and dried in vacue with $\rm CaCl_2$. Oxygen was not exchanged between $\rm UO_4$ and the hydration water. Preliminary experiments were in good agreement with Ref. 3 (C. A. Kraus, Manhattan Project, Report A-281, A-328 (1942); AM-7 (1944)) and Ref. 4 (J. E. Boogs, M. El-Chehabi, J. Am. Chem. Soc., 79, 4258 (1957)). They showed the following results: the formation of the orange-colored compound $\rm U_2O_7$ by heating $\rm UO_4 \cdot 2H_2O$ gradually up to 195°C. $\rm U_2O_7$ reacts vigorously with water or $\rm H_2SO_4$ solutions, oxygen is liberated, and $\rm UO_3$, or a uranyl salt is formed, respectively. $\rm U_2O_7$ is slowly decomposed, oxygen is liberated, and red $\rm UO_3$ forms by heating between 200 and 400°C. The $\rm U_2O_7$ content decreased in the solid phase during

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25337 S/020/61/138/006/013/019 B103/B215

Investigation of higher oxides and ...

the decomposition of $\rm UO_4 \cdot 2H_2O$ at 195°C as the oxygen pressure was reduced. At 15 mm Hg and less it reached 50 %. Higher oxygen pressure also elevated the pressure of water vapor which partly decomposed $\rm U_2O_7$. Oxygen was liberated from $\rm H_2O_2$ by permanganate during isotope analysis, peroxide oxygen was liberated from $\rm U_2O_7$ by the action of water, and the oxygen of $\rm U_3O_8$ was transformed by heating with $\rm HgCl_2 + Hg(CN)_2$ in $\rm CO_2$. In water, oxygen was analyzed by a method already described (Ref. 11: A. I. Brodskiy Khimiya izotopov (Chemistry of isotopes) 2-ye izd., Izd. AN SSSR, 1957, p. 117). The oxygen liberated during the stepwise decomposition of $\rm UO_4^{18}$ 2 2 4 has the same isotope composition as the initial $\rm H_2O_2^{18}$ and as the peroxide oxygen obtained from $\rm U_2O_7$ which escapes by treating the solid phase with acidified water. The $\rm O_1^{18}$ content in this oxygen is much higher than its average content in the solid phase. Thus, the O atoms in $\rm UO_4$ and $\rm U_2O_7$ are not bound in the same way. Peroxide oxygen preserves its structural isolation in these oxides, and is the first Card 3/6

25337 \$/020/61/138/006/013/019 B103/B215

Investigation of higher oxides and...

X

to be separated in thermal decomposition. When heating uranium peroxide up to 195° C, 1.9 moles of water per 1 mole of $\rm UO_4$ are liberated. This water contains 13-24~% of 0^{18} of the initial $\rm H_2O_2$. From this fact the authors conclude that heavy uranium peroxide does not have the perhydrate structure $\rm UO_3$ - $\rm H_2O_2^{18}$ - $\rm H_2O$ (contrary to Ref. 8: C. Duval, Anal. Chem. Acta, 3, 337 (1949)). By thermal decomposition of light uranium peroxide prepared in $\rm H_2O^{18}$, water is formed with an $\rm O^{18}$ content always higher than that of the solid phase. The portion of peroxide oxygen entering water which is separated up to 195° C is the larger, the smaller the $\rm U_2O_7$ residue not decomposed into a lower oxide. Hence, the authors assume that the absorption of lower amounts of peroxide oxygen by the water is due to the isotope exchange with $\rm UO_3$. The authors proved this experimentally. The calculated and determined $\rm O^{18}$ contents confirmed this assumption. Therefore, the authors conclude that uranium tetroxide is a genuine $\rm UO_4 \cdot 2H_2O$ peroxide. Corresponding to this structure, it does not exchange Card $\rm 4/6$

Investigation of higher oxides and...

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oxygen with the $\mathrm{H_2O_2}$ solution. The decomposition of $\mathrm{U_2O_7}$ is terminated between 400 and 420°C , and no more oxygen is liberated. The orangecolored solid phase turns red, and does no longer separate oxygen during its interaction with water. Its composition approaches that of ${\tt UO}_3$. The liberation of oxygen again sets in at 450-500°C and lasts until 700-800°C is reached. The solid phase then turns dark-green and its composition approaches that of $0_3^{\circ}0_8$. The isotope composition of liberated oxygen does not change between 350 and 700°C, and remains equal also in the final ${\rm U_{3}0_{8}}$. The authors assume this to reflect the equivalence of the cxygen atoms in \mathtt{UO}_3 and $\mathtt{U}_3\mathtt{O}_8$, which is confirmed radiographically. From the results, they conclude that both ${\tt UO_4} \cdot {\tt 2H_2}{\tt 0}$ and $\mathbf{U}_2\mathbf{0}_7$ are genuine peroxides whose atoms of peroxide oxygen are structurally isolated. UO3 and U308, however, have an oxide structure. There are 2 tables and 12 references: 3 Soviet-bloc and 10 non-Soviet-bloc. Two references to English-language publications are given in the body of Card 5/6

1

25337

Investigation of higher oxides and ...

s/020/61/138/006/013/019 B103/B215

the abstract, the third reads: Ref. 10: M. Anbar, S. Guttman, Intern. J. Appl. Rad., 5, 233 (1959).

ASSOCIATION: Institut fizicheskoy khimii im. L. V. Pisarzhevskogo Akademii nauk USSR (Institute of Physical Chemistry imeni L. V. Pisarzhevskiy of the Academy of Sciences UkrSSR)

SUBMITTED:

March 6, 1961

Card 6/6

ROYTER, Vladimir Andreyevich; BRODSKIY, AI., akademik, otv. red.; POKROVSKAYA, Z.S., red.; DAKHNC, Yu.B., tekhn. red.

[Introduction to the theory of kinetics and catalysis] Vvedenie v teoriiu kinetiki i kataliza. Kiev, Izd-vo Akad. nauk USSR, (MIRA 16:1) 1962. 110 p.

1. Akademiya nauk Ukr. SSR (for Brodskiy). (Kinematics) (Catalysis)

BRODSKIY, A.I.; GOL'DENFEL'D, I.V.; GRAGEROV, I.P.

Isotopic analysis of oxygen in water by the persulfate method. Zhur.anal.khim. 17 no.72893-895 0 62. (MIRA 15:12)

1. Institute of Physical Chemistry, Academy of Sciences, Ukrainian S.S.R.

(Oxygen-Isotopes) (Water-Analysis)

BRODSKIY, A.I.; POKHODENKO, V.D.; ALEKSANKIN, M.M.; GRAGEROV, I.P.

Formation and decomposition of cumene hydroperoxide in H20¹⁸. Zhur.ob.khim. 32 no.3:758-760 Mr '62. (MIRA 15:3)

1. Institut fizicheskoy khimii imeni L.V.Pisarzhevskogo AN USSR. (Hydroperoxide) (Oxygen--Isotopes)

BRODSKIY, A.I.; ALEKSANKIN, M.M.; GRAGEROV, I.P.

Mechanism of pyruvic acid oxidation by hydrogen peroxide.

Zhur.ob.kiim. 32 no.3:829-833 Mr '62. (MIRA 15:3)

1. Institut fizicheskoy khimii imeni L.V.Pisarzhevskogo AN USSR. (Pyruwic acid) (Hydrogen peroxide)

BRODSKIY, A.I.; VYSOTSKAYA, N.A.

Methanism of phenol hydroxylation and anthracene oxidation by peroxide compounds studied with the aid of 013. Zhur.ob.khim. 32 no.782273-2278 Il 162. (MIRA 15:7)

l. Institut fizicheskoy khimil imeni L.V.Pisarzbovskogo AN Ukrainskoy SSR.
(Phenols) (Hydroxylation) (Anthracene) (Oxidation)

POKHODENKO, V.D.; GANYUK, L.N.; BRODSKIY, A.I.

Rearrangement of the free radical of oxidized ionol. Dokl.AN SSSR 145 no.4:815-817 Ag 62. (MIRA 15:7)

Institut fizicheskoy khimii im. L.V.Pisarzhevskogo AN USSR.
 Chlen-korrespondent AN SSSR (for Brodskiy).
 (Cresol) (Radicals (Chemistry))

BRODSKIY, A.I., POKHODENKO, V.D.; GANYUK, L.N.

Study of the transformations of radicals during the oxidation of 2,6-di-(1,1'-dimethylalkyl)-4-methylphenols. Zhur.strukt.khim. 4 no.2:210-215 Mr-Ap '63. (MIRA 16:5)

1. Institut fizicheskoy khimii imeni L.V.Pisarzhevskogo AN UkrSSR, Kiyev.

(Phenol) (Oxidation) (Radicals (Chemistry))

BRODSKIY, Aleksandr Il'ich; CHERNYAK, V.S., red.; TIKHONOVA, I.A., red.izd-va; KHENOKH, F.M., tekhm. red.

[Using propane and butane in the cutting and welding of metals] Primenenie propana i butana pri rezke i svarke metallov. Moskva, Izd-vo M-va kommun.khoz.RSFSR, 1963. 110 p. (MIRA 17:2)

S/020/63/148/006/016/023 B117/B186

AUTHORS:

Pokhodenko, V. D., Ganyuk, L. N., Yakovleva, Ye. A., Shatenshteyn, A. I., Brodskiy, A. I., Corresponding Member AS USSR

ZITLE:

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 148, no. 6, 1963, 1314 - 1315

TEXT: Experiments with a tagged para-methyl group were made in order to prove the rearrangement of the phenoxy radical (I) in benzyl radical (II) which was observed during the oxidation of 2.6-di-tert-butyl-4-methylphenol (ionone) by means of deuterium tagging. Ionone with deuterium in the methyl group was obtained by hydrogen isotopic exchange with the KND₂ solution in liquid ND₃ under comparatively rigid conditions. Ionone-CD₃(0.1 M solution in C₆H₆) turns yellow during the oxidation with PbO₂ in vacuo. In the infra-red spectra of the oxidized ionone-CD₃, dissolved in CCl₄, not only the frequencies corresponding to the phenol and the C=O group Card 1/2

E.p.r. spectrum and rearrangement ...

S/020/63/148/006/016/023 B117/B186

(1610 cm⁻¹) were observed, but also a band (2692 cm⁻¹) corresponding to the OD group which confirms the regrouping (I)→(II). The e.p.r. spectrum of the phenoxy radical of ionone-CD₃ was found to consist of 9 lines. Intensity ratio of these lines: 1:4.4:13:23:26:23:13:4.5:1; the splitting between the components is equal and is a₁ = 1.8 oe. This spectrum corresponds to that determined previously for the phenoxy radical of ionone-CH₃
(A. I. Brodskiy, V. D. Pokhodenko, L. N. Ganyuk, Zhurn. strukturn. khim (in press); A. L. Buchachenko, M. B. Neyman, DAN, 139, 916 (1961)). In the case of continuous oxidation it is not changed, as was observed in the spectrum of the phenoxy radical of ionone-CH₃. After 1.5 hr it passes into

ASSOCIATION: Institut fizicheskoy khimii im. L. V. Pisarzhevskogo Akademii nauk USSR (Institute of Physical Chemistry imeni L. V. Pisarzhevskiy of the Academy of Sciences UkrSSR); Fiziko-khimioheskiy institut im. L. Ya. Karpova (Physicochemical Institute imeni L. Ya. Karpov)

a singlet with a width of 2.4 ce. There is 1 figure.

SUBMITTED: November 4, 1962 Card 2/2

POKHODENKO, V.D.; GANYUK, L.N.; BRODSKIY, A.I.

Radicals, products of the thermal decomposition of substituted cyclohexadienone peroxide. Dokl. AN SSSR 149 no.2:321-323 Mr '63. (MIRA 16:3)

Institut fisicheskoy khimii im. L.V.Pisarzhevskogo AN UkrSSR.
 Chlen-korrespondent AN SSSR (for Brodskiy).

 (Cyclohexadienone) (Radicals (Chemistry))

BRODSKIY, A.I.; LUNENOK-BURMAKINA, V.A.

Nature of surface platinum oxides formed during the anode discharge of hydrogen peroxide. Dokl. AN SSSR 151 no.6:1358-1359 Ag '63. (MIRA 16:10)

1. Institut fizicheskoy khimii im. L.V.Pisarzhevskogo AN UkrSSR. 2. Chlen-korrespondent AN SSSR (for Brodskiy).

BRODSKIY, A.I.; VSOTSKAYA, N.A.

"Isotopenuntersuching über den Mechanisums der Hydroxylierung von Benzol and seinen Derivaten durch Peroxyde"

Report submitted for the COSPAR Fifth International Space Science Symposium, Florence, Italy, 8-20 May 1964.

DEGTYAREV, L.S.; GANYUK, L.N.; GOLUBENKOVA, A.M.; BRODSKIY, A.I.

Electron paramagnetic resonance spectra and the transmission of the influence of substituents in anion radicals of paranitrodiphenyls. Dokl. AN SSSR 157 no.6:1406-1409 Ag '64. (MIRA 17:9)

1. Institut fizicheskoy khimii im. L.V. Pisarzhevskogo AN UkrSSSR. 2. Chlen-korrespondent AN SSSR (for Brodskiy).

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ACCESSION NR: AP5015494	UR/0286/65/000/008/0027/0027 621.317.783.
AUTHOR: Akhiyezer, A. N.; Brodskiy	CATE STATE STATES A 49 THE STATES
TITLE: Film bolometer for optical 21, No. 170085	transmission lines? Class
SOURCE: Byulleten' izobreteniy i to	varnykh znakov, no. 8, 1965, 27
TOPIC TAGS: bolometer, film bolomet	er
ABSTRACT: The proposed film bolomes in the millimeter and submillimeter at the focus of a collecting lens. of electromagnetic wave energy, it made of parallel strips of absorbing so that its plane is perpendicular to the subject of	wavelength ranges is positioned. To achieve effective absorption as designed in the form of a grid material. The grid is placed to the direction of wave propaga-
tion, while the planes of the indivi- plane of electric-field polarization	dual strips are parallel to the
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BRODSKIY, A. I.

BRODSKIY, A. I.

Congresde Leningrad May-June, 1924; Rev. meta. 22,

206-9 (1925)

B-iron and the specific heats of pure iron.

CA: 19-2471/5



BRODSKIY, A. I.

BRODSKIY, A. I. J. Russ. Met. Soc. 1925, I, 165-73; J. Inst. Metals 34, 408-9
The specific heats of metals and their melting points.

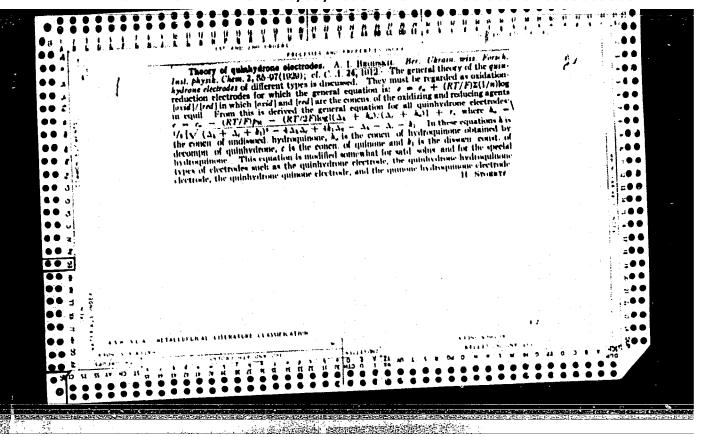
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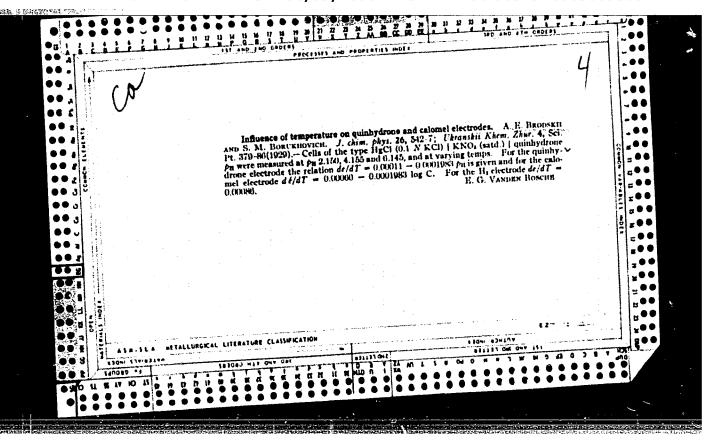
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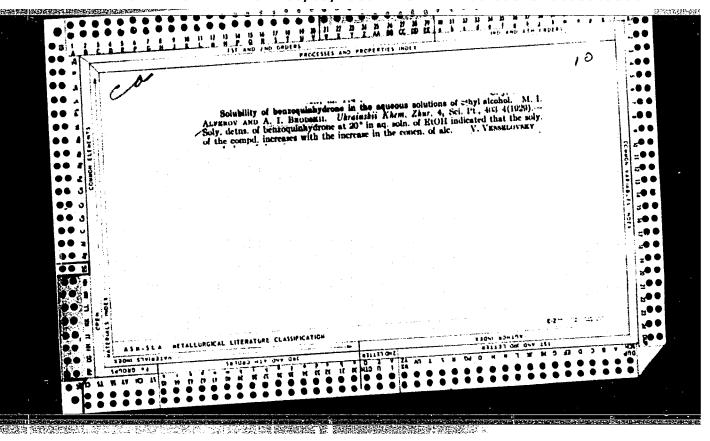
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BRODSKIY, A. I.

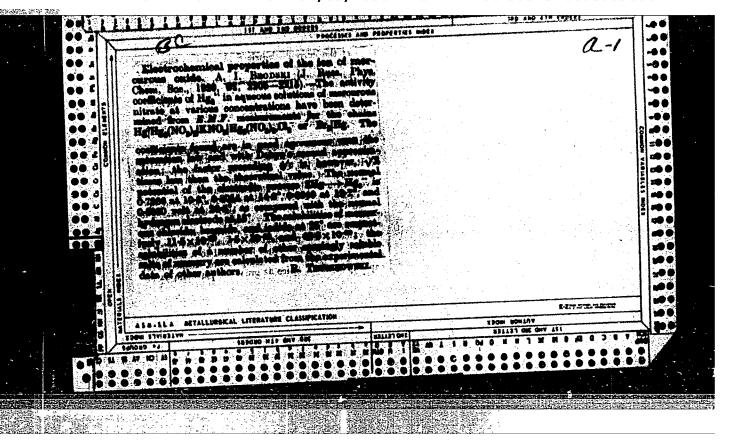
BRODSKIY, A. I. J. Russian Met. Soc. <u>1926</u>, No. 1, Sec. L, 7-22 Critical points and heat capacities of pure iron. CA: 20-2809/9

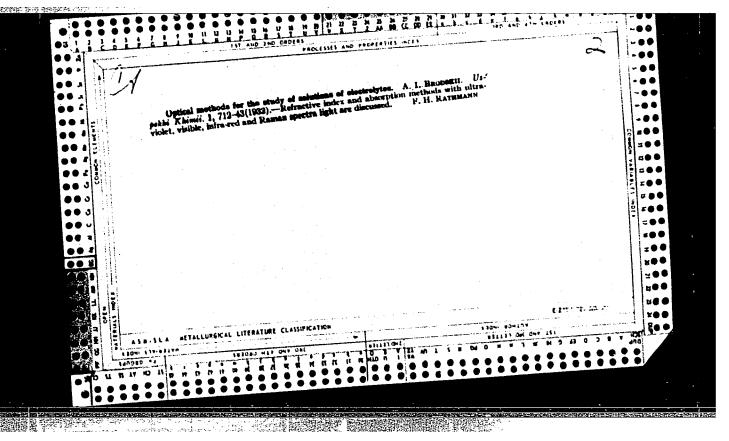


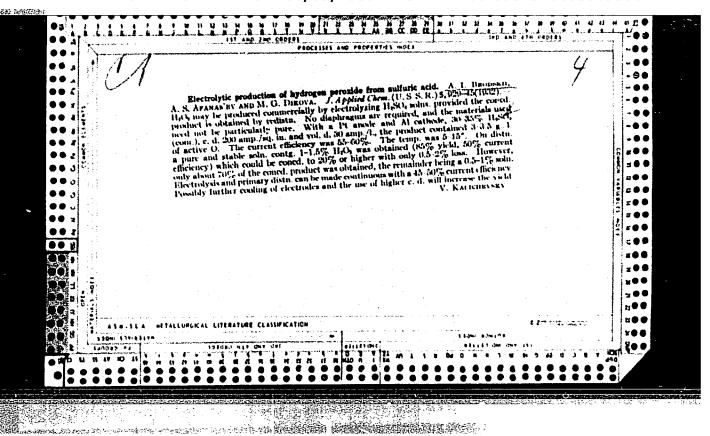




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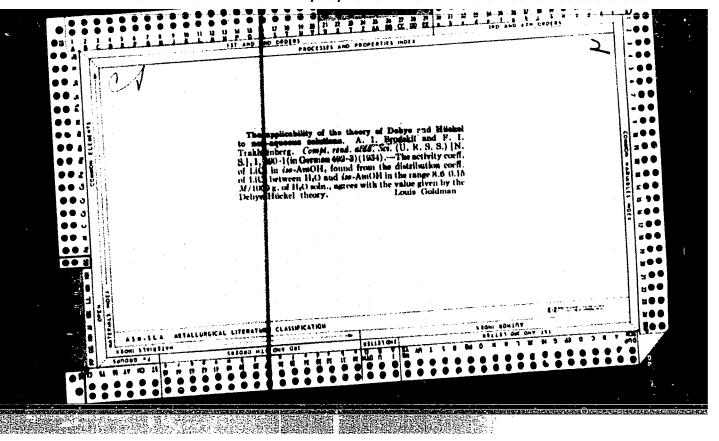




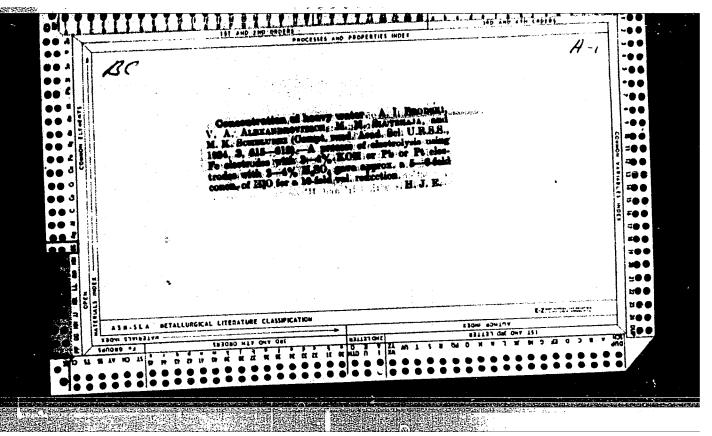
BRODSKTY, Aleksandr Il'ich

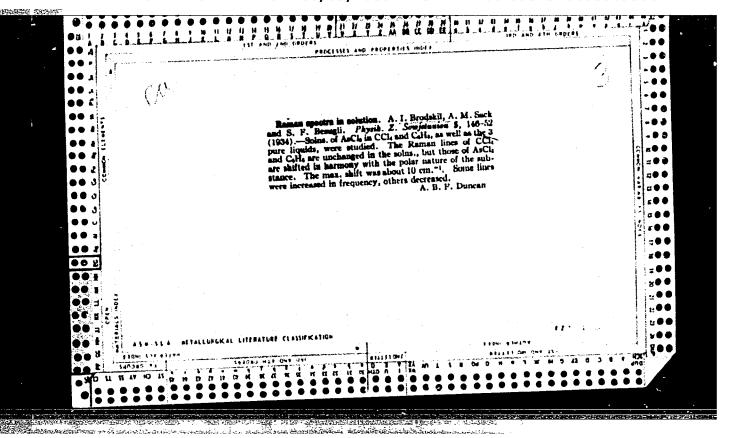
"A Modern Theory of Electrolytes," (Sovremennaya teoriya elektrolitov), Leningrad, 1934.

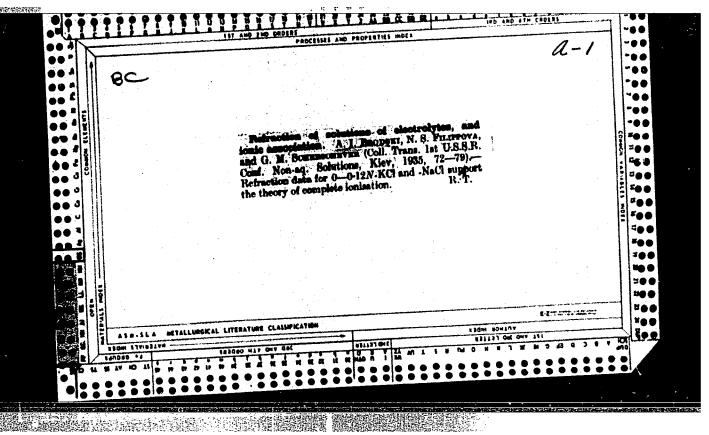
Bol'shaya Sovetskaya Entsiklopediya, Vol. VI., 2nd ed., Moscow, 1949.

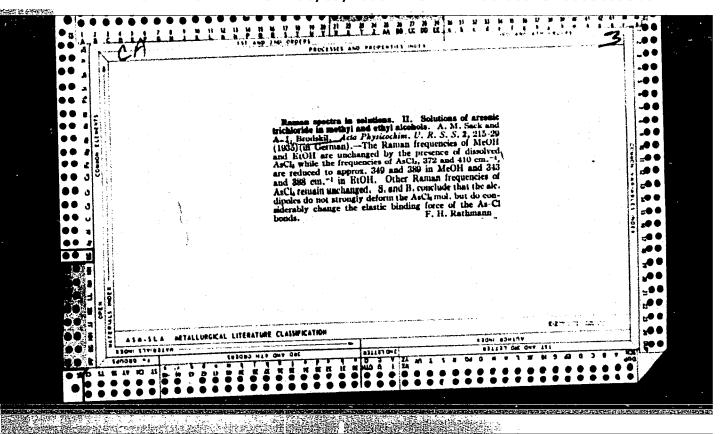


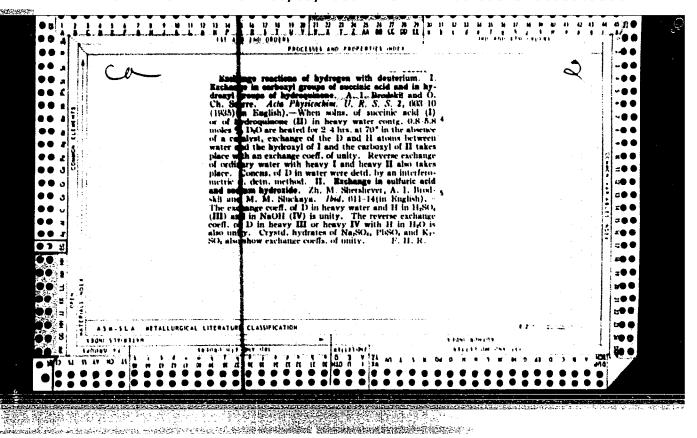
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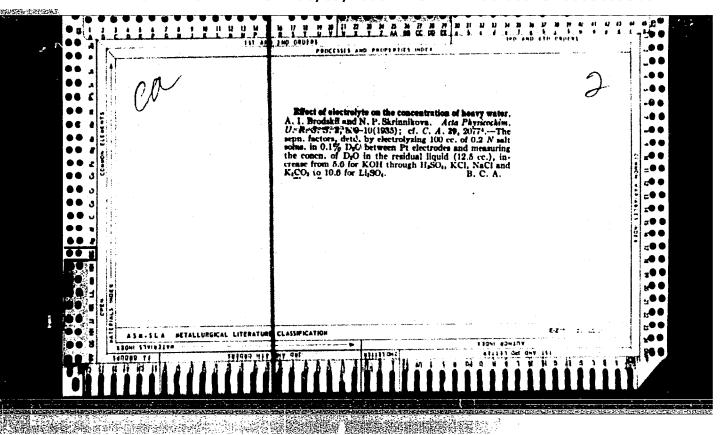


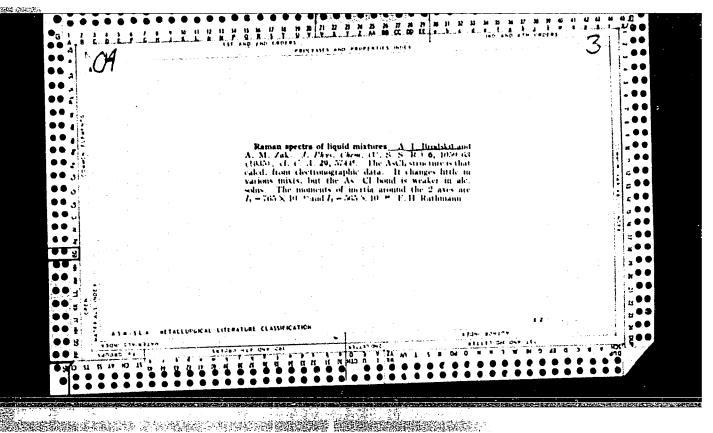


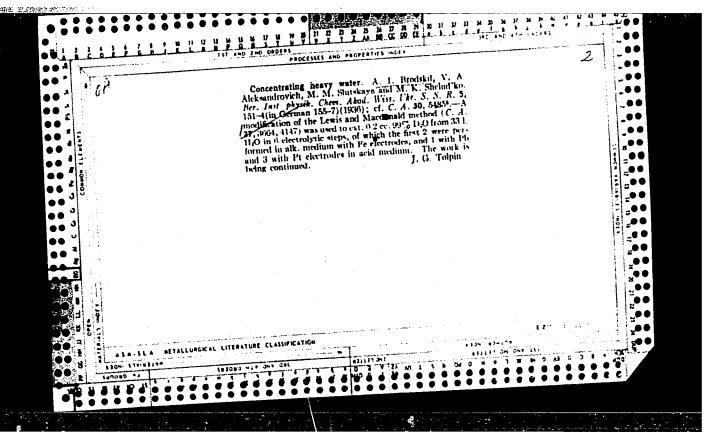


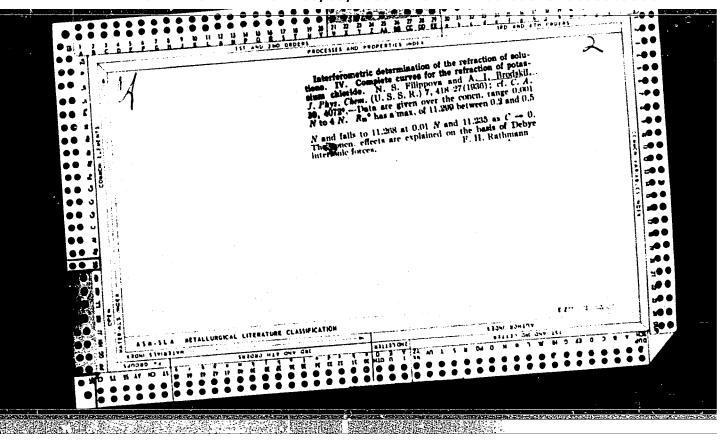


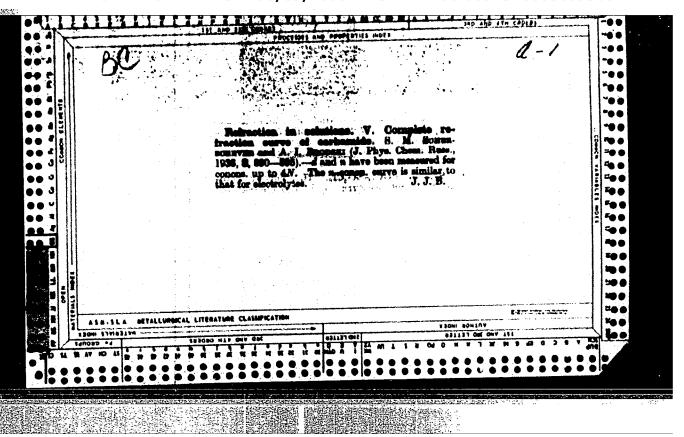


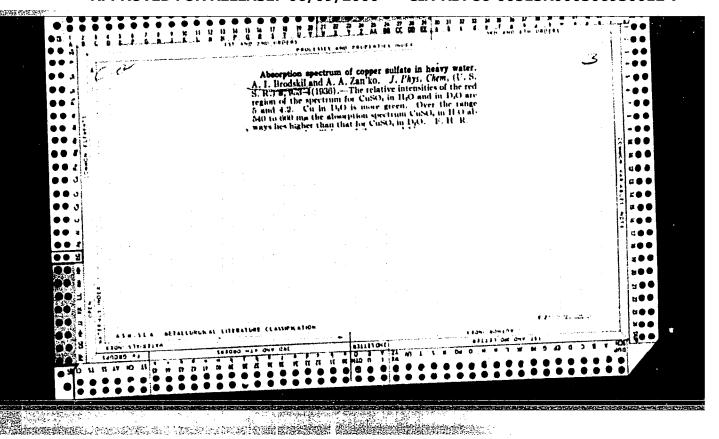


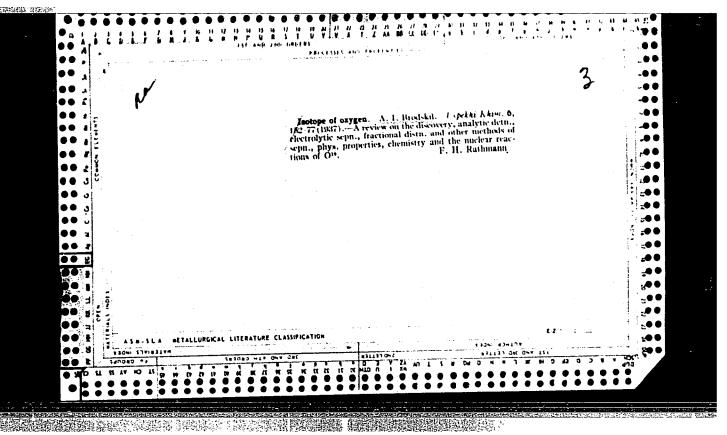


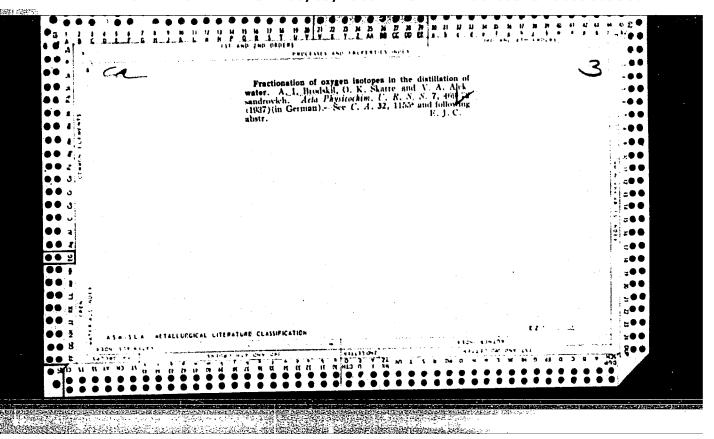


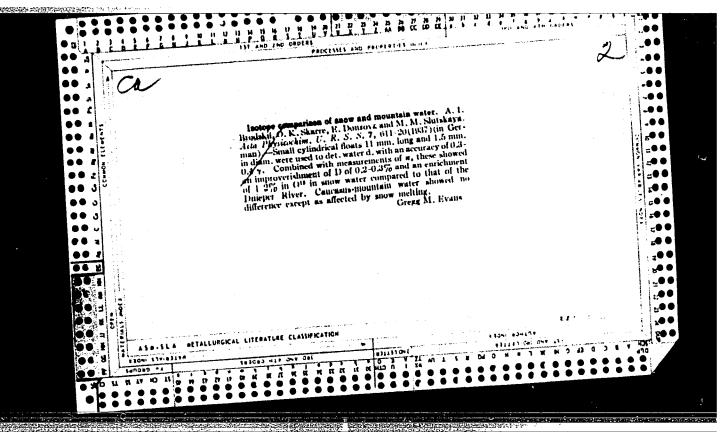


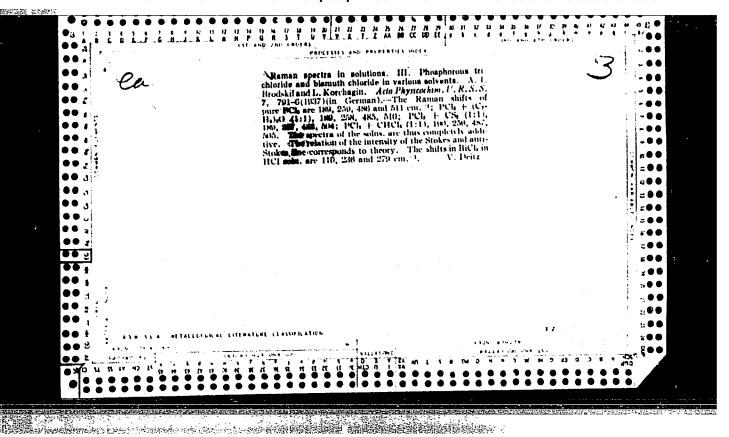


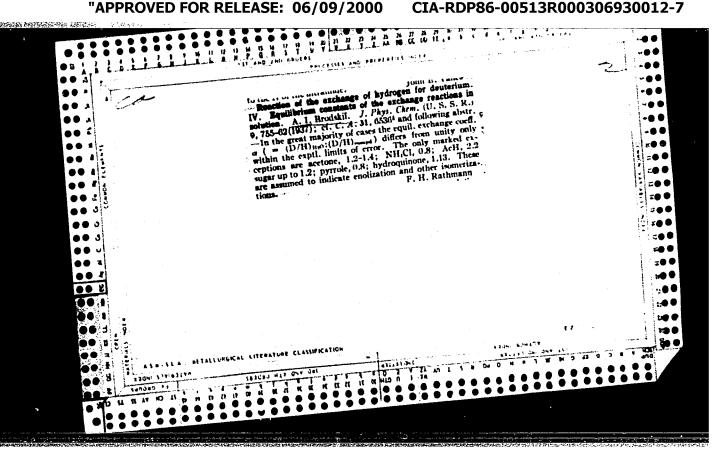


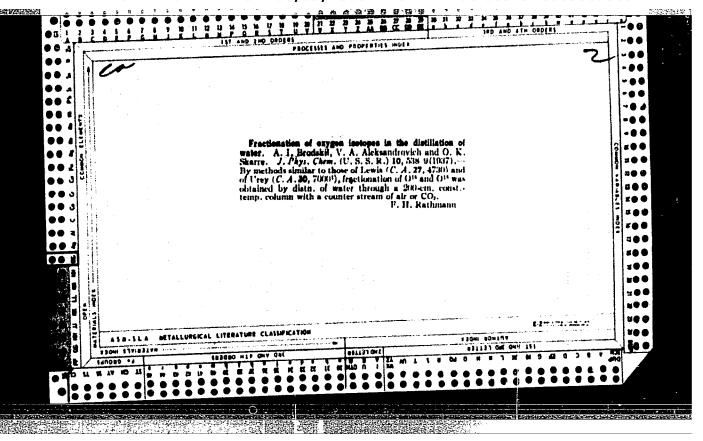


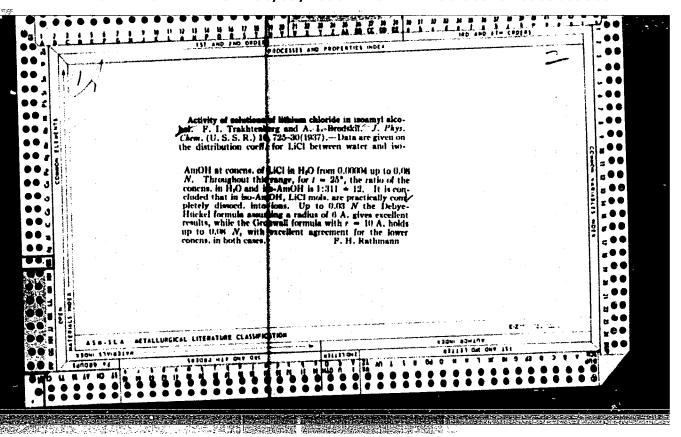


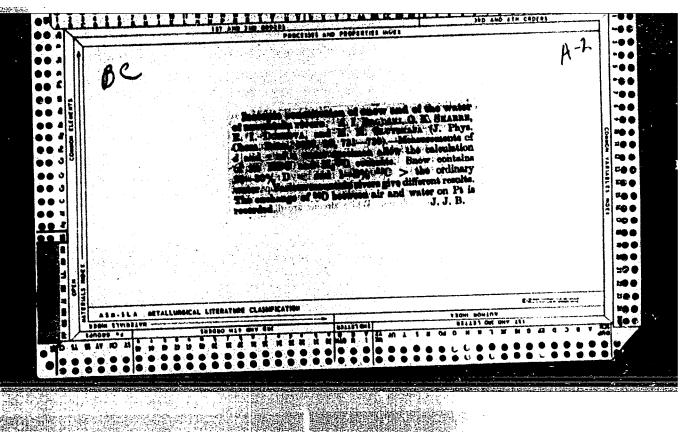


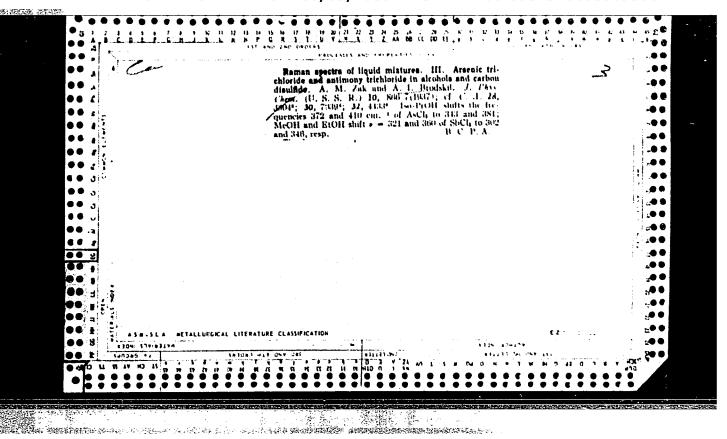








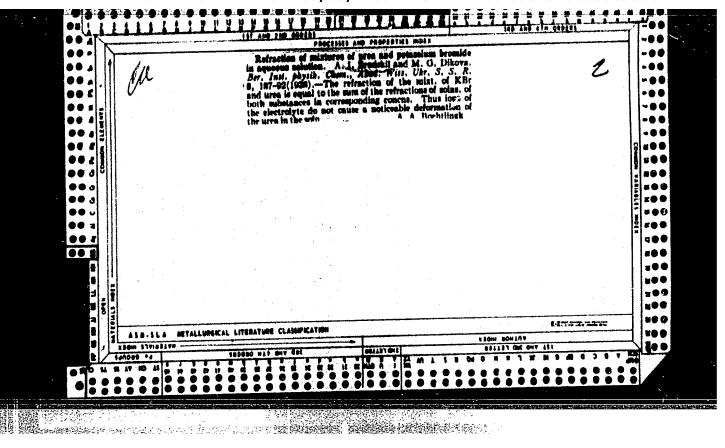


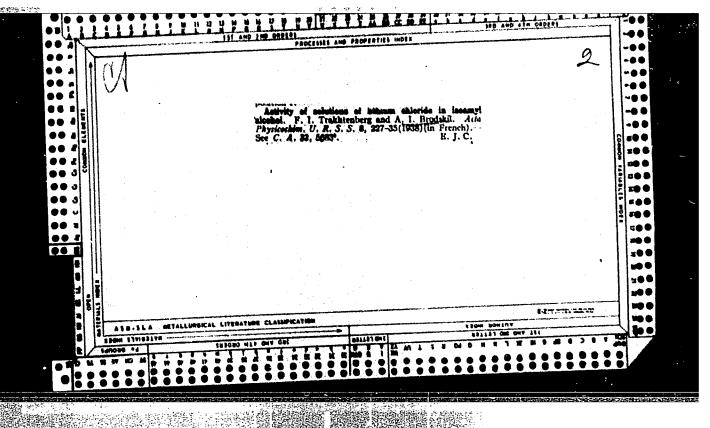


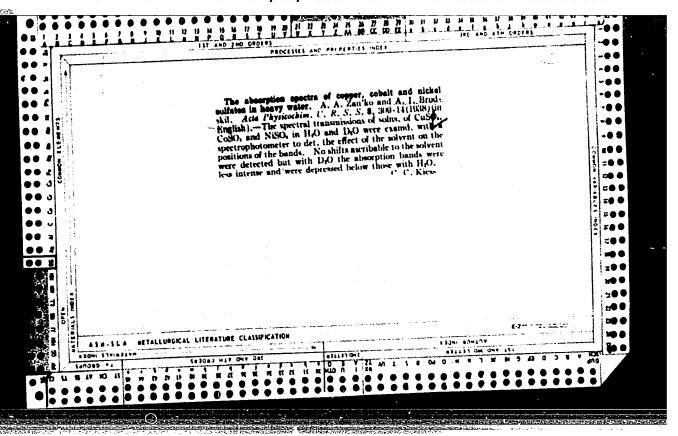
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